NASA TECHNICAL NOTE

NASA TN D-3236

c. 1

NASA TN D-3236

LOAN COPY: B
AFWL (W
KIRTLAND AF
0079808
TECH LIBRARY KAFB, NM

DEPENDENCE OF SURFACE CONDUCTIVITY OF SODIUM CHLORIDE ON THE CHEMICAL NATURE OF THE SURFACE

by Charles E. May and John P. Jayne

Lewis Research Center

Cleveland, Ohio

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • FEBRUARY 1966

TECH LIBRARY KAFB, NM
0079808

DEPENDENCE OF SURFACE CONDUCTIVITY OF SODIUM CHLORIDE ON THE CHEMICAL NATURE OF THE SURFACE

By Charles E. May and John P. Jayne

Lewis Research Center
Cleveland, Ohio

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

For sale by the Clearinghouse for Federal Scientific and Technical Information
Springfield, Virginia 22151 – Price $1.00

DEPENDENCE OF SURFACE CONDUCTIVITY OF SODIUM CHLORIDE ON THE CHEMICAL NATURE OF THE SURFACE

by Charles E. May and John P. Jayne

Lewis Research Center

SUMMARY

The surface conductivity S of sodium chloride was measured near room temperature as a function of the partial pressure of water vapor P, absolute temperature T (over a 20° range), and surface treatments. For all specimens, $\log S = \log S_0 + \frac{\alpha' P}{T^{\sim 11}}$, where S_0 is the extrapolated value of surface conductivity at zero water pressure and α' is a proportionality constant. The value of α' for treated surfaces is in general about 40 percent greater than the value for as-cleaved surfaces. The values of S_0 vary as follows:

$$S_0 \text{ (deuteroxide surface)} > S_0 \text{ (hydroxide surface)} \gg S_0 \text{ (carbonate surface)}$$

$$S_0 \text{ (compact)} \gg S_0 \text{ (melt-grown single crystal)} \geq S_0 \text{ (natural crystal)}$$

The work confirms the existence of hydroxide and carbonate groups on the surface of sodium chloride.

INTRODUCTION

Recent work (refs. 1 to 4) has shown that even at room temperature, chemical reactions occur on the surface of sodium chloride (NaCl) when exposed to certain gases. When NaCl is exposed to water (H_2O) vapor, hydrolysis occurs; when exposed to moist carbon dioxide (CO_2), amounts of carbonate (or bicarbonate) equivalent to a monolayer can be formed. Such a coverage by carbonate (or bicarbonate) should have a large effect on surface properties, particularly surface conductivity.

The purpose of this investigation was to search for such an effect because its existence would substantiate the presence of the carbonate layer as well as increase our understanding of surfaces. Fortunately, the room temperature surface conductivity of some ionic crystals (including NaCl) is relatively high in the presence of H_2O vapor (refs. 5 to 8). Moreover, the bulk conductivity of NaCl is negligible at room temperature. Thus, conditions are favorable for the

desired measurements.

The scope of this work includes the determination of the surface conductivity of various NaCl samples as a function of the partial pressure of water vapor, temperature, and surface treatments.

EXPERIMENTAL

The 13 NaCl samples investigated were of 4 types: melt-grown single crystals (optical grade), naturally occurring single crystals, compacted powders (ground from melt-grown crystals), and compacted granules (reagent grade). The compacts were made at room temperature (ref. 9) by hydrostatic pressing (50 000 psi). The single crystals were cleaved rectangular solids (ranging from 3 to 10 mm on a side) while the compacts were in the form of cylinders (roughly 13 mm in diameter and from 4 to 9 mm thick).

Conductivities were determined for the as-cleaved (and as-cut) specimens as well as for the specimens after various chemical surface treatments. The treatments included (1) exposure to the vapor from 12 normal hydrochloric acid (HCl) for about 100 hours (air present), (2) exposure to 100 percent H_2O humidity for about 10 minutes (in conductivity cell, air absent), (3) exposure to CO_2 at 60 percent humidity for about a day (air present), and (4) exposure to 100 percent deuterium oxide (D_2O) humidity for about 10 minutes (in conductivity cell, air absent). Treatment (4) was used only on specimen 14; furthermore, in connection with such D_2O treatments, D_2O was also used as the vapor during some of the conductivity determinations.

The apparatus shown schematically in figure 1 proved to be adequate for all the measurements. The specimen was held in a glass vacuum chamber between two flat platinum contacts, the lower one being spring loaded. Stopcocks permitted the chamber to be isolated from an adjoining manometer, water reservoir (properly degassed), and vacuum pump. The temperature of the specimen could be varied slightly through the use of a heating tape; to prevent interference with conductivity measurements, an isolation transformer was required with it. The difference between the specimen temperature and room temperature was measured with a thermocouple in close proximity to the crystal (<5 mm). Contact between the specimen and thermocouple was found to interfere with conductivity measurements.

The chamber with the specimen in position was initially evacuated to about 0.01 torr and degassed overnight. Water vapor was then admitted and the system allowed to stand about 30 seconds to ensure equilibrium. The pressure was then read with the aid of a cathetometer, and the conductivity was measured as follows. A known potential (1.35-V mercury cell) in series with a standard precision high resistance (10^{10} ohms) was placed across the specimen. The potential across the standard resistance was then measured with a vibrating reed electrometer so that the current, voltage drop across the sample, and finally the conductivity of the sample could be calculated. The entire system had to be well shielded and grounded as indicated in figure 1. The range of measureable conductivities was from about 10^{-14} to 10^{-10} mho. By multiplying the

measured conductivities by the ratio of sample length to perimeter, the specific surface conductivities were obtained.

After the initial measurement, more water vapor was admitted, and the pressure and conductivity were remeasured. The process was continued so as to obtain a run of about 8 experimental points over the measurable range of conductivities. The temperature was measured to $\pm 0.1^{\circ}$ and appeared to be essentially constant during a run. The chamber was reevacuated, and another run of 8 points was obtained. The first two runs were done at about 23° C. For most of the samples, the measurements were repeated at about 30° C and again at about 39° C. In none of the measurements was any evidence of polarization of the crystals detected. It should also be noted that the value of the partial pressure of water over a saturated solution of NaCl was never exceeded during a run; thus, condensation of water on the specimen was prevented.

Preliminary experiments were performed to substantiate that the conductivity measured was truly due to the surface. In these, a continuous narrow band of insulating plastic material was painted around a single crystal essentially parallel to the contact ends and allowed to dry; this electrically isolated the two halves of the surface. Then the conductivity of the crystal was measured perpendicular to the band at H_2O vapor pressures from 0 to 18 torr. The fact that no conductivity was measurable even at 18 torr indicates that any conductivity measured for crystals without insulating bands must be due to surface conductance.

DATA HANDLING

Before the effect of surface treatments can be discussed in detail, it is necessary to ascertain that the effects noted are not due to other variables, such as pressure and temperature. For the 13 specimens tested, no conductivity was observable ($<10^{-14}$ mho) at 0-torr water vapor pressure; however, when sufficient H_2O pressure was present, the conductivity could be measured. It should be noted that the attainment of a constant conductivity reading was almost instantaneous, and thus the effect of any possible diffusion of H_2O into the bulk is shown to be negligible; this is additional evidence that the conductance is taking place on the surface.

The dependence of the specific surface conductivity $S_P^{[t]}$ on the vapor pressure of water P is shown in figure 2 and can be expressed as follows:

$$\log S_P^{[t]} = \log S_0 + \alpha[t] \cdot P \tag{1}$$

where $\log S_0$ and $\alpha[t]$ are the intercept and slope, respectively. Such a dependence is typical of all 13 specimens investigated. In appendix A, the significance of equation (1) is discussed. Using the least squares method, the indices of correlation of the three curves in figure 2 are 0.9997 for 24.5° C, 0.9998 for 32.0° C, and 0.9957 for 41.5° C. Simkovich (ref. 8) claims that $\log S$ for NaCl is proportional to $\log P$; however, we found by replotting his data (fig. 5 of ref. 8) that equation (1) yields a slightly better

fit than the equation that Simkovich proposes.

As illustrated in figure 2, the slope decreases rapidly with increasing temperature. In figure 3, the value of the slope $\alpha[t]$ is shown to be inversely proportional to roughly the tenth power of the absolute temperature T. The average value of this power from all the temperature dependency determinations was 11.4±2.8. Thus, equation (1) can be reexpressed roughly as follows:

$$\log S_P^{[t]} = \log S_0 + \frac{\alpha' P}{T^{11}} \tag{2}$$

where α' is temperature independent. This reciprocal power dependence (even though the power varied somewhat) is a better representation of the data than the usual type of temperature expressions (i.e., $\alpha[t] = \alpha_0 - BT$ or $\ln \alpha[t] = \ln \alpha_0 + B/T$ where α_0 and B are constants). Although appendix A indicates there may be some theoretical significance to the form of the pressure dependence, the form found for the temperature dependence seems to be merely empirical. However, the relationship found does allow $\alpha[t]$ to be corrected very adequately for slight changes in temperature (appendix B); this was the primary purpose in determining the dependence on temperature. Referring again to figure 2, the intercept ($\log S_0$) can be seen to be essentially independent of temperature over the small range (about 20° C) investigated. The least squares method gives the following values for $\log S_0$ in figure 2: -19.65 for 24.5° C, -19.41 for 31.2° C, and -19.69 for 41.5° C.

The surface treatments had a detectable effect on the slope at 23° C, $\alpha[23]$ (table I; method of calculation in appendix B); however, the effects were not consistent with the type of treatment. Thus, the effects must be attributed to changes in the surface other than those of a chemical nature (e.g., the growth of small crystallites observed on single crystals after treatments). One generality, however, could be made: the values of $\alpha[23]$ for as-cleaved (and as-cut) samples were consistently lower than the average value of $\alpha[23]$ for all treatments (table II). The roughly 40 percent increase in the value of $\alpha[23]$ with treatment can be attributed also to the existence of these crystallites on the surfaces because they could contribute to the short circuit mechanism discussed in appendix A. It should be noted that the value of $\alpha[23]$ for all as-cleaved (and as-cut) samples is essentially a constant.

The actual conductivity, however, shows a dependence on the type of surface treatment indicating that a chemical effect is involved. In figure 4, the effect of HCl on a melt-grown crystal is illustrated; conductivity is enormously increased with the treatment. In figure 5, the effect of CO_2 is shown; conductivity in general is decreased slightly. For ease of comparing all the data, one can make use of the value $\log S_{10}^{[23]}$ the logarithm of the conductivity at 23° C, and 10-torr H_2O vapor pressure (table III; method of calculation in appendix B).

As the data in table III is discussed, the following generalities will become apparent:

For melt-grown crystals,

$$S_{10}^{[23]}(H_2O \text{ treated}) \approx S_{10}^{[23]}(HCl \text{ treated}) \gg S_{10}^{[23]}(\text{as cleaved}) > S_{10}^{[23]}(CO_2 \text{ treated})$$

For natural single crystals,

$$S_{10}^{[23]}(H_2O \text{ treated}) \approx S_{10}^{[23]}(HCl \text{ treated}) \approx S_{10}^{[23]}(\text{as cleaved}) \gg S_{10}^{[23]}(CO_2 \text{ treated})$$

For compacts,

$$S_{10}^{[23]}(H_2O \text{ treated}) \approx S_{10}^{[23]}(HCl \text{ treated}) \gg S_{10}^{[23]}(CO_2 \text{ treated}) > S_{10}^{[23]}(\text{as cleaved})$$

The order in which treatments were carried out had little effect on the results, except that after many treatments, specimens sometimes failed to show the expected effect (particularly for specimen 18). For simplicity of discussion of the data, the initial treatments will be discussed first.

The effect of HCl on as-cleaved melt-grown crystals (increase in conductivity) can be seen for specimens 10, 11, 13, and 15 (table III). The same type of effect can be noted for compacts (specimens 21, 22, and 24). However, the effect of HCl on as-cleaved natural crystals is to decrease the conductivity (specimens 16 and 17). The effect of H_2O (100 percent humidity) was to increase the conductivity (specimen 14) in much the same manner as the HCl. The effect of CO_2 on all as-cleaved crystals (and presumably as-cut compacts) was to decrease the conductivity by a detectable amount (table III, specimens 11 and 18).

The effect of secondary treatments (the second treatment of each specimen) substantiates the general relationships. A secondary treatment with HCl of H_2O-treated specimen 14 has no effect. Secondary treatments using H_2O on specimens first treated with HCl (specimens 10, 11, 13, 15, 16, and 17) show no consistent effect. Secondary CO_2 treatments of H_2O-treated specimen 23 and of HCl-treated specimens 21, 22, and 24 decrease the conductivity enormously (but not to a value lower than the as-cleaved specimens). Secondary H_2O treatment (specimen 12) and secondary HCl treatment (specimen 18) of CO_2-treated specimens increase the conductivity by a large factor. Proceeding through table III, one sees that subsequent treatments also support the above generalities stated for the value of $S_{10}^{[23]}$. One set of such treatments should be particularly noted (final treatment of specimens 16 and 17); HCl treatments of previously CO_2-treated natural crystals do increase the conductivity.

The conductivity of the specimen treated with D_2O showed the same type of dependence on vapor pressure and temperature as did specimens with other treatments (see eqs. (1) and (2)). Thus, a comparison can again be made using the values $\alpha[23]$ and $S_{10}^{[23]}$ as calculated according to appendix B; the values are listed in table IV. The values for $\alpha[23]$ appear unusually constant; the values of $\alpha[23]$ for measurements in D_2O vapor are over 10 percent higher than

values for measurements in H_2O vapor. However, this variation is far less than the usual scatter in table II and thus may not necessarily be significant. The data in table IV also show the large difference between S_{10}[23] for D_2O vapor and the value for H_2O vapor. The conductivity of NaCl in D_2O vapor is about 8 times greater than that of NaCl in H_2O vapor.

INTERPRETATION

Based on the observed dependency of conductivity on treatments as well as recent investigations by Otterson, et al. (refs. 1 to 4), the chemistry of the surface of NaCl is interpreted to be as follows. Surfaces of NaCl when exposed to CO_2 (60 percent humidity) are hydrolyzed and become contaminated with carbonate. Values of conductivity after CO_2 treatments are therefore characteristic of a carbonate surface; such surfaces are found to possess for the most part the lowest conductivity of the surfaces measured. Since as-received NaCl (except natural material) contains some sodium hydroxide (NaOH) (over 10 ppm), surfaces are easily converted to a carbonate-type surface by interaction with CO_2 present in the atmosphere (even at relatively low humidity). Depending on the amount of exposure, an as-cleaved crystal could show a conductivity which approaches the low value for a carbonate surface. Deliberate treatment of such as-cleaved crystals with CO_2 undoubtedly would add more carbonate and thus decrease the conductivity as was observed. As-cleaved natural crystals containing no detectable NaOH do not react with the CO_2 present in the air (perhaps due to low humidity) and thus do not exhibit the low conductivity characteristic of carbonate surfaces. For compacts, the as-cut specimens exhibit a lower conductivity than specimens after subsequent CO_2 treatments; this is interpreted to indicate that the CO_2 treatment used was not sufficient to convert surfaces of the compacts completely to carbonate-type ones. The exposure of the powder (before compaction) to the air (containing CO_2) appears to be a more effective treatment for the formation of a carbonate-type surface.

Treatment of totally or partially carbonate-covered surfaces by H_2O (100 percent humidity) would remove the carbonate by solution-type ablation and hydrolysis of the surface. The resultant surface could be classed as a hydroxide-type (OH^-) surface. Treatment of the carbonate-type surface with HCl would result in a NaCl-type surface; however, during the conductivity measurements exposure to even low H_2O vapor pressure can cause hydrolysis, resulting in an OH^- surface. Thus, both H_2O and HCl treatments lead to the same type of surface and are expected to have the same effect upon conductivity, as is found experimentally. This OH^- surface exhibits a relatively high conductivity. It should be noted that once an OH^- surface is formed it should not be exposed to air lest the CO_2 present therein reacts to form a carbonate surface.

Following the above type of reasoning, surfaces of as-cleaved natural crystals (containing no OH^- and thus no carbonate) should show conductivity similar to those with HCl treatments, because with exposure to H_2O vapor in the conductivity cell, the surfaces would convert to the OH^- type. Actually, the surfaces show a conductivity slightly different (higher) from the OH^- type; however, this

is not unexpected because the natural crystals have a far different overall purity (lower) than optical or reagent-grade material.

Because hydrolysis occurs readily on a NaCl surface, it is logical that treatment of an OH^- surface with D_2O even below the saturation point should cause through chemical exchange the formation of a deuteroxide (OD^-) surface possessing different conductivity than the OH^- type. Experimentally it is found that the OD^- surface has the higher conductivity of the two. Thus one can attribute the difference between the values of $S_{10}^{[23]}$ for H_2O and D_2O to the surface chemical condition and not to the nature of the molecules absorbed on the surface.

One may say, in general, that treatments have the effect of generating either a carbonate, OH^-, or OD^- surface. Even though a NaCl surface exists, its conductivity is not measurable in the present investigation because of the hydrolysis occurring during the actual conductivity measurements (H_2O being present). Table V is a summary of the data (average $S_{10}^{[23]}$ for H_2O and D_2O to comparison of $S_{10}^{[23]}$ is equivalent to a comparison of S_0 (as explained in appendix B, last paragraph), one may write

$$S_0 \text{ (OD}^- \text{ surface)} > S_0 \text{ (OH}^- \text{ surface)} \gg S_0 \text{ (carbonate surface)}$$

An additional comparison that can be made is one between the values of $S_{10}^{[23]}$ for the various specimens. To ensure chemical uniformity, the specimens should be compared under the same chemical condition, (e.g., after the first HCl treatments (table III). No dependence of $S_{10}^{[23]}$ on the shape of the specimen was found, but there was a dependence on the type of specimen. All single crystals (S.C.) have much the same value for $S_{10}^{[23]}$, with the melt-grown specimens having slightly higher values of $S_{10}^{[23]}$ than the natural material. The scatter within either group is not large except for specimen 18. The compacts exhibit conductivities over 2 orders of magnitude greater than the single crystals; this can be attributed to the large roughness factors undoubtedly present in such compacts. The comparison of the conductivities as a function of the type of specimen can also be made with the aid of the summary in table V. Finally, the comparisons can be expressed in terms of S_0 (see appendix B, last paragraph):

$$S_0 \text{ (compact)} \gg S_0 \text{ (melt-grown S.C.)} \geq S_0 \text{ (natural S.C.)}$$

Although the purpose of this paper is not to discuss the mechanism of the observed surface conductivity, a few comments should be made. The conclusions of this research are not dependent on the type of conduction involved (ionic or electronic); thus, the present work cannot be used to prove conclusively whether an ionic or electronic mechanism is involved. However, ionic conduction might involve polarization, and this was not observed. Furthermore, we

believe that the difference in conductivity between an OH^- surface and an OD^- surface can more easily be explained in terms of band theory than by simple ionic conductance. On the other hand, sintering experiments supply evidence that ionic mobility takes place on NaCl at room temperature (refs. 10 and 11) when H_2O or HCl vapor is present.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, December 1, 1965.

APPENDIX A

INTERPRETATION OF EXPERIMENTALLY FOUND EQUATION

It is desirable to give further interpretation to equation (1)

$$\log S_P^{[t]} = \log S_0 + \alpha[t]\cdot P$$

The first observation is of course that S_0 can be interpreted as the conductivity of a water-free surface. As water is absorbed, aggregates of water having less resistance than the underlying surface act as short-circuit elements and decrease the overall resistance. (If absorbed water acts only as a short-circuit medium, simple adsorption of D_2O should have essentially the identical effect on conductivity as does the adsorption of H_2O.) To a first approximation, the resistance $R_P^{[t]}$ of the crystal may be expressed as

$$R_P^{[t]} = R_0(1 - f) \tag{A1}$$

where R_0 is the resistance of a water-free surface and f is the fraction of surface containing the short-circuit elements. Then, by rearrangement and substitution of conductivity for resistance, one can obtain:

$$\log S_P^{[t]} = \log S_0 - \log(1 - f) \tag{A2}$$

Combining equations (1) and (A2),

$$\alpha[t]\cdot P = -\log(1 - f) \tag{A3}$$

Differentiating,

$$\alpha[t] = \left(\frac{\partial f}{\partial P}\right)_T \frac{1}{2.303(1 - f)} \tag{A4}$$

or

$$\left(\frac{\partial f}{\partial P}\right)_T = 2.303\ \alpha[t](1 - f) \tag{A5}$$

Equation (A5) is a reasonable relationship; it states that the rate of change of the short-circuit fraction with pressure is proportional to the uncovered surface. Empirically, $\alpha[t]$ is shown to be a very rapidly changing function of temperature.

APPENDIX B

CALCULATION OF $S_{10}^{[23]}$

For ease of comparison of the abundant data, it was convenient to calculate and compare a single value of $\alpha[t]$ and a single value of $S_P^{[t]}$ for all treatments. The values selected were those at 23° C and 10-torr water pressure, $\alpha[23]$ and $S_{10}^{[23]}$. A comparison of the values of S_0 would have had the advantage of being temperature independent (see text proper), but S_0 is a highly extrapolated value (see fig. 2); in contrast, $S_{10}^{[23]}$ is an interpolated value. The interpolation procedure will now be described.

The values of $\alpha[t]$ and S_0 were calculated for all nominally 23° C (296.2° K) runs by the least squares method; the temperature of these runs never varied more than 2° from 23° C. The value of $\alpha[23]$ could therefore be calculated:

$$\alpha[23] = \alpha[t] \cdot \left(\frac{T}{296.2}\right)^{11} \tag{B1}$$

The use of T^9 or T^{13} in place of T^{11} would have made only a 3 percent difference in the value of $\alpha[23]$. Using $\alpha[23]$, $S_{10}^{[23]}$ can be found as follows:

$$\log S_{10}^{[23]} = \log S_0 + 10 \cdot (\alpha[23]) \tag{B2}$$

This equation is equivalent to

$$\log S_{10}^{[23]} = \log S_P^{[23]} + 10(\alpha[23] - \alpha[t]) \tag{B3}$$

and thus does not involve the extrapolation errors inherent in the value of S_0.

A comparison of the effects of chemical treatment on the values of $S_{10}^{[23]}$ is equivalent to a comparison involving S_0 because the value of $\alpha[t]$ is not a function of the chemical treatments (see first full paragraph after eq. (2)).

REFERENCES

1. Otterson, Dumas A.: On the Presence of NaOH in Crystalline NaCl. J. Chem. Phys., vol. 33, no. 1, July 1960, pp. 227-229.

2. Otterson, Dumas A.: Influence of Room-Temperature Atmospheric Reaction Products on the Ductility of Sodium Chloride Single Crystals. J. Chem. Phys., vol. 38, no. 7, Apr. 1, 1963, pp. 1481-1486.

3. Otterson, Dumas A.; and Davies, Myron O.: Study of Carbonate Impurity in Surface Region of Sodium Chloride Crystals. NASA TN D-2434, 1964.

4. Otterson, Dumas A.; and Davies, Myron O.: Method of Determining Carbonate Ion in Surface of Crystalline Solids by Means of Mass Spectrometric Gas Analysis. NASA TN D-2764, 1965.

5. Uhara, Itsuro; and Nakamura, Morizumi: Adsorption of Solvent Vapor by the Solute Crystal. Bull. Chem. Soc. Japan, vol. 12, no. 5, 1937, pp. 227-233.

6. Jayne, John P.: Effects of Humidity on the Surface Conductivity of Sodium-Chloride Single Crystals. Bull. Am. Phys. Soc., Ser. II, vol. 7, no. 3, Mar. 26, 1962, paper D 8, p. 179.

7. Gheorghita-Oanchea, Candida; and Cristea, Paul: Observation on the Influence of the Air and Water Vapor at Different Pressures on the Electrical Conductivity of NaCl Single Crystals. Bull. Inst. Politeh Bucuresti (Rumania), vol. 24, no. 4, Oct.-Dec. 1962, pp. 43-48.

8. Simkovich, George: The Surface Conductivity of Sodium Chloride Crystals as a Function of Water Vapor Partial Pressure. J. Phys. Chem., vol. 67, no. 5, May 1963, pp. 1001-1004.

9. May, Charles E.; Grimes, Hubert H.; and Lad, Robert A.: Ductile Ceramics. II - Introductory Study of Ductility in Polycrystalline Sodium Chloride and Magnesium Oxide. NASA TN D-76, 1959, p. 2.

10. Moffat, J. B.; and McIntosh, R.: The Preparation and Sintering of Finely Divided Sodium Chloride. II. Can. J. Chem., vol. 35, no. 12, Dec. 1957, pp. 1511-1521.

11. Rudham, R.: Sintering of Evaporated Films of Sodium Chloride. Trans. Faraday Soc., vol. 59, 1963, pp. 1853-1859.

TABLE I. - EFFECT OF TREATMENT ON $\alpha[23]$

[Specimens were melt-grown single crystals; treatments were performed in the sequence presented; a blank space indicates that a particular treatment was omitted from the sequence.]

Treatment	$\alpha[23]$, $torr^{-1}$	
	Specimen 10	Specimen 11
As cleaved	0.47	0.62
HCl	.62	.55
H_2O	.56	.54
CO_2	.59	.69
H_2O	.46	
CO_2	.54	
HCl	.77	.72
H_2O		.73
CO_2	.65	.61
HCl	.78	.91
H_2O	.70	.78

TABLE II. - VALUES OF $\alpha[23]$

Specimen	Type	$\alpha[23]$, $torr^{-1}$		Increase, percent
		As cleaved	Average for all treatment	
10	Melt-grown single crystal	0.47	0.62	35
11	↓	.62	.69	12
12		.58	.73	25
13		.60	.63	5
14		.52	.84	62
15		.58	.83	44
16	Natural single crystal	.46	.72	58
17	Natural single crystal	.49	.74	52
18	Natural single crystal	.77	.76	-1
21	Compact (melt-grown material)	.48	.73	55
22	Compact (melt-grown material)	.50	.71	44
23	Compact (melt-grown material)	.42	.68	62
24	Compact (reagent grade)	.47	.70	48
Average		0.54	0.72	44

TABLE III. - VALUES OF $\log S_{10}^{[23]}$ [a]

Treatment	$-\log S_{10}^{[23]}$ for specimen indicated												
	Single crystals (melt-grown)						Single crystals (natural)			Compacts (melt-grown material)			Compact (reagent grade)
	10	11	12	13	14	15	16	17	18	21	22	23	24
None (as cleaved)	13.68	14.34	14.28	13.71	13.79 [b](13.84)	14.51	12.68	12.28	8.73	13.12 [b](12.86)	12.62	12.56	11.87
H_2O					13.17[1]							9.88[1]	
CO_2			14.81[1]						11.90[1]			12.52[2]	
HCl	11.97[1]	12.99[1]		13.08[1]	13.14[2]	12.76[1]	13.25[1]	13.46[1]	9.79[2]	10.31[1]	10.17[1]	11.14	9.57[1]
H_2O	12.70[2]	12.70[2]	13.85[2]	12.16[2]		13.54[2]	12.60[2]	12.85[2]	11.52				
CO_2	13.50	13.59	14.52	13.69	13.94	15.11	15.40	14.65	11.60	11.06[2]	11.35[2]	11.14	10.05[2]
H_2O	12.78		13.85	13.16				12.84	11.40				
CO_2	13.61		14.52	13.85				14.25					
HCl	11.86	12.18	12.10	12.40	12.40	12.60	12.22	13.05	12.36	9.64	11.00	7.74	8.78

[a]Treatments were performed in the sequence presented; a blank space indicates that a particular treatment was omitted from the sequence; for easier reference, [1] indicates initial treatment and [2] indicates second treatment.

[b]Numbers in parenthesis are rerun values.

TABLE IV. - COMPARISON OF THE EFFECTS

OF H_2O AND D_2O (SPECIMEN 14)

Treatment	Vapor present during measurement	$\alpha[23]$, $torr^{-1}$	$-\log S_{10}^{[23]}$
100 percent D_2O humidity	D_2O	0.61	12.16
(a)	H_2O	.55	13.17
100 percent H_2O humidity	H_2O	.54	13.05
(a)	D_2O	.61	12.31
100 percent D_2O humidity	D_2O	.60	12.32
(a)	H_2O	.55	12.84
100 percent H_2O humidity	H_2O	.51	13.01

[a]No additional treatment.

TABLE V. - AVERAGE VALUES OF $\log S_{10}^{[23]}$

Condition of surface	$-\log S_{10}^{[23]}$ for various types of samples		
	Melt-grown single crystals	Natural single crystals[a]	Compacts
As cleaved	14.05	12.48	12.60
Carbonate surface	14.16	15.02	11.22
OH^- surface	12.82	13.04	10.30
OD^- surface	12.26		

[a]Specimen 18 not used in averages.

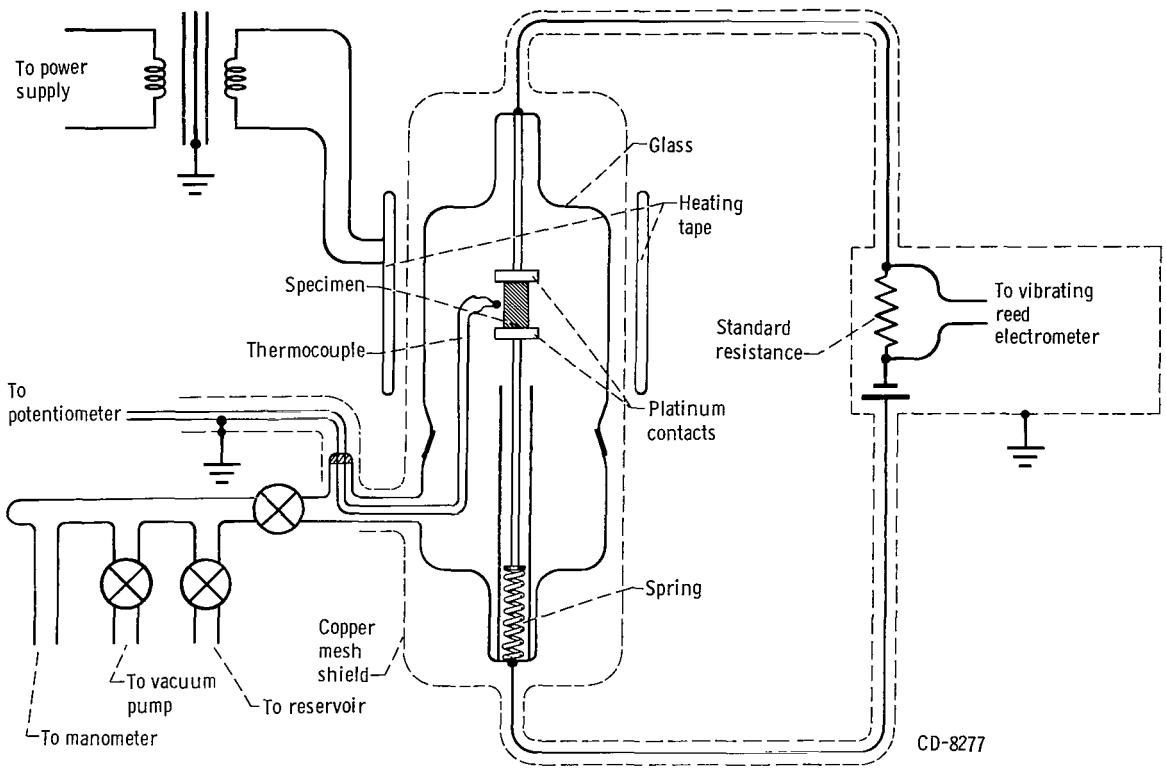

Figure 1. - Schematic of conductivity apparatus.

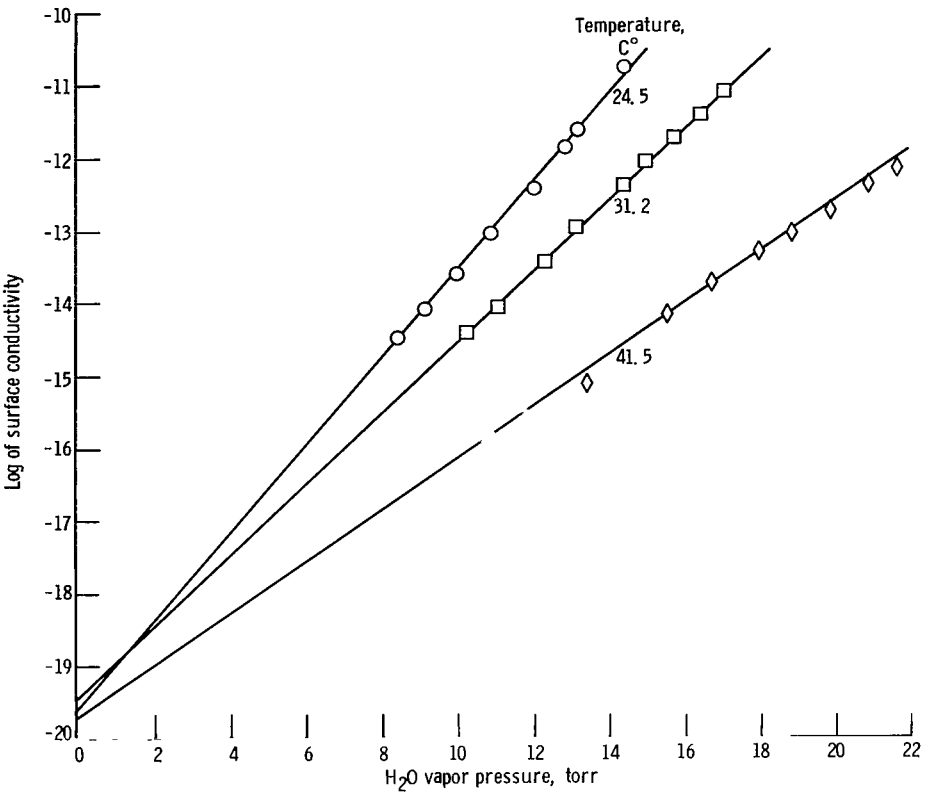

Figure 2. - Conductivity as function of pressure (specimen 12; H_2O treated).

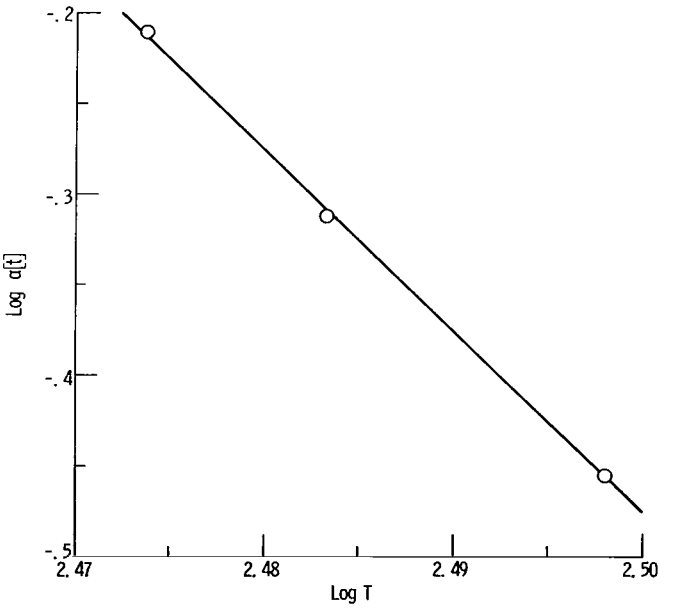

Figure 3. - Dependence of α[t] on temperature (specimen 12; H_2O treated).

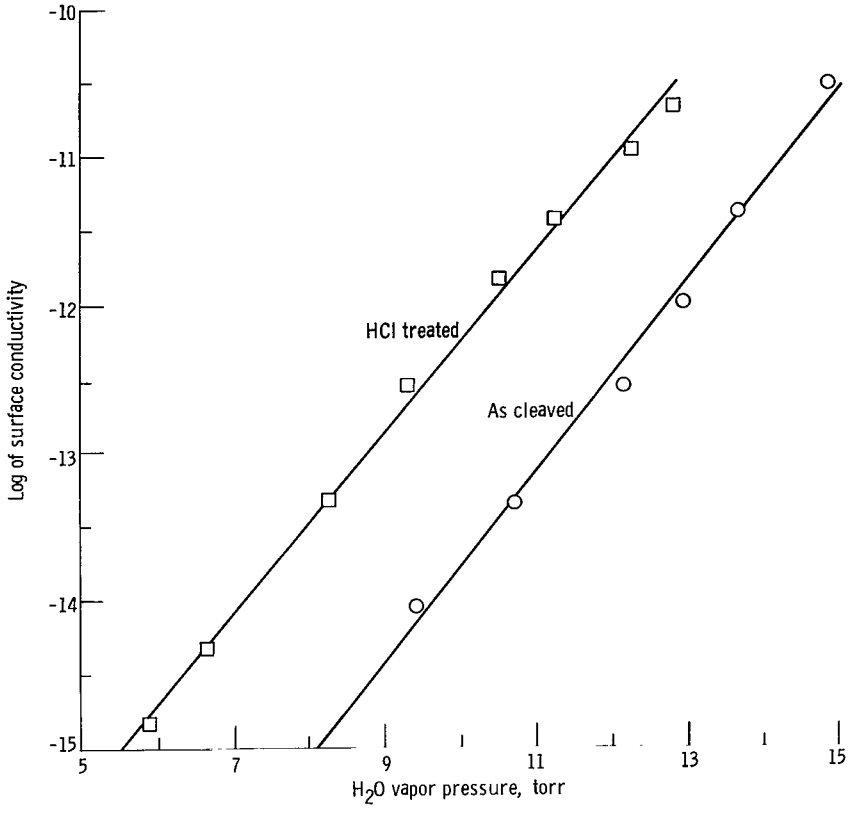

Figure 4. - Effect of HCl treatment (specimen 11; temperature, 24.1° C).

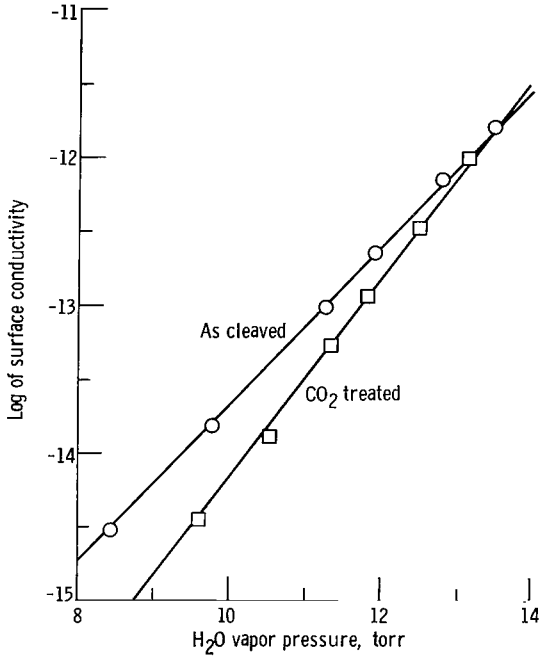

Figure 5. - Effect of CO_2 treatment (specimen 12; temperature, 24.0° C).

NASA-Langley, 1966 E-3158

"The aeronautical and space activities of the United States shall be conducted so as to contribute . . . to the expansion of human knowledge of phenomena in the atmosphere and space. The Administration shall provide for the widest practicable and appropriate dissemination of information concerning its activities and the results thereof."

—NATIONAL AERONAUTICS AND SPACE ACT OF 1958

NASA SCIENTIFIC AND TECHNICAL PUBLICATIONS

TECHNICAL REPORTS: Scientific and technical information considered important, complete, and a lasting contribution to existing knowledge.

TECHNICAL NOTES: Information less broad in scope but nevertheless of importance as a contribution to existing knowledge.

TECHNICAL MEMORANDUMS: Information receiving limited distribution because of preliminary data, security classification, or other reasons.

CONTRACTOR REPORTS: Technical information generated in connection with a NASA contract or grant and released under NASA auspices.

TECHNICAL TRANSLATIONS: Information published in a foreign language considered to merit NASA distribution in English.

TECHNICAL REPRINTS: Information derived from NASA activities and initially published in the form of journal articles.

SPECIAL PUBLICATIONS: Information derived from or of value to NASA activities but not necessarily reporting the results of individual NASA-programmed scientific efforts. Publications include conference proceedings, monographs, data compilations, handbooks, sourcebooks, and special bibliographies.

Details on the availability of these publications may be obtained from:

SCIENTIFIC AND TECHNICAL INFORMATION DIVISION

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Washington, D.C. 20546